

Understanding the origin for wide voltage window of microporous carbon electrode with oxygen-containing defect by modulating surface chemistry

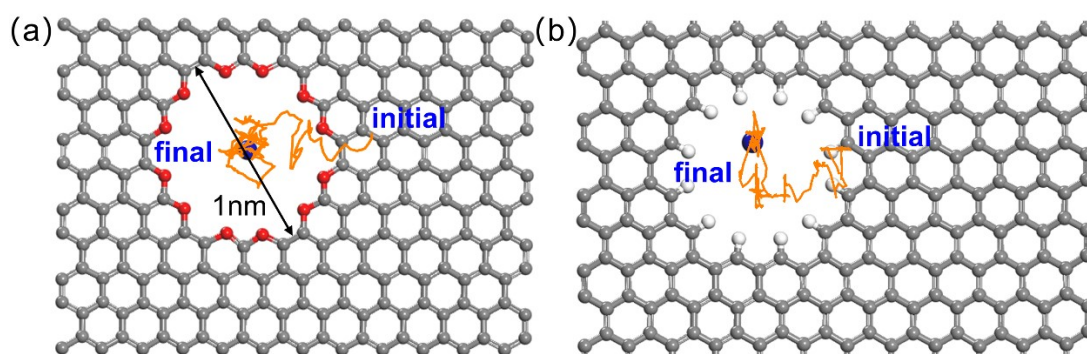


Figure S1. ~5 ps trajectory of one Na^+ on (a) O-pore surface and (b) H-pore surface.

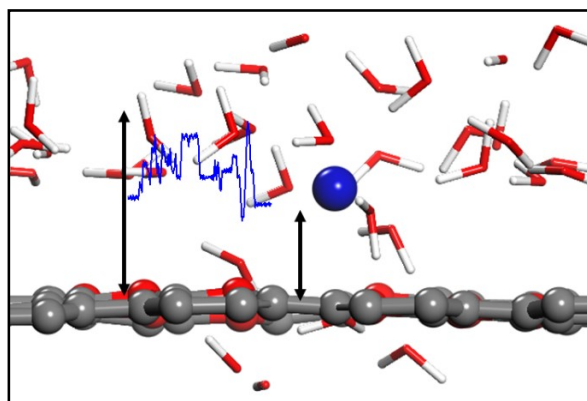


Figure S2. ~5 ps trajectory of one Na^+ above the O-pore surface.

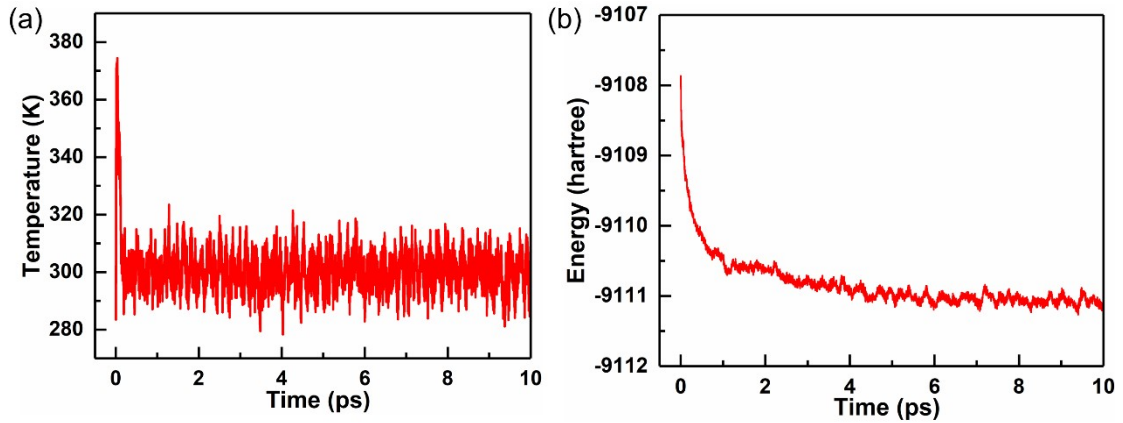


Figure S3. (a) Temperature and energy evolutions versus simulation time.

Section S1. Theoretical aspects of Metadynamics. During ab initio molecular dynamics (AIMD), various geometries are sampled as a function of simulation time t and can be described using a generalised coordinate $q(t)$. In metadynamics, a bias potential is, on top of that, added to the unknown free energy surface $F(q)$ along a few chosen geometric parameters (distance, angles, or any sort of quantities that depend on q) called collective variables s_i . For the sake of simplicity, the ensemble of the selected d collective variables will be referred to as the vector \vec{s} .

The bias potential is progressively built during AIMD through the periodic addition (stride τ) of small amounts of free energy that takes the form of gaussians. This history-dependent potential $V(\vec{s}, t)$ then writes:

$$V(\vec{s}, t) = \sum_{k < \frac{t}{\tau}} W(k\tau) \exp \left(- \sum_i \frac{(s_i - s_i(q(k\tau)))^2}{2\sigma_i^2} \right)$$

where W is the height of the Gaussians and σ_i the width along the direction of collective variable s_i . In the limit of long simulation times, the bias potential converges and is related to the free energy surface projected along the selected collective variables.

$$V(\vec{s}, t \rightarrow \infty) = -F(\vec{s}) + \text{constant.}$$

Section S2. Work function calculation

For modelling a charged interface, Na atom was introduced into the water layer, which could separate into protons and electrons and vary the surface charge and potential. According to the definition, work function is the difference between the vacuum energy level and fermi level. In this work, we calculate electrostatic potential of more than 10 typical structures from the last 5 ps by single-point energy calculation. As shown in Figure 3c, the corresponding electrostatic potential in the range from 32 to 35 Å of x-axis represents the vacuum energy level, because this part is vacuum layer in the model (Figure 1f). Meanwhile, the value of fermi level directly obtains from the simulation results.

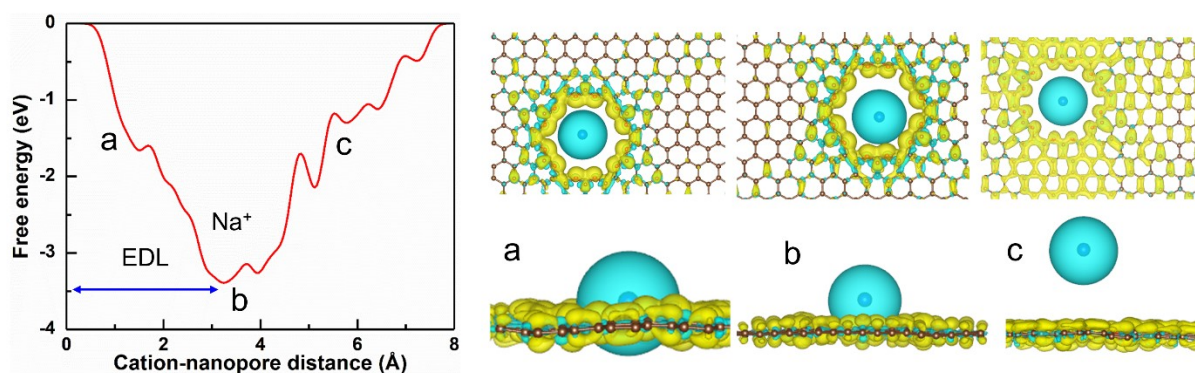


Figure S4. Charge differential density profile of the interface with Na^+ located at different positions.

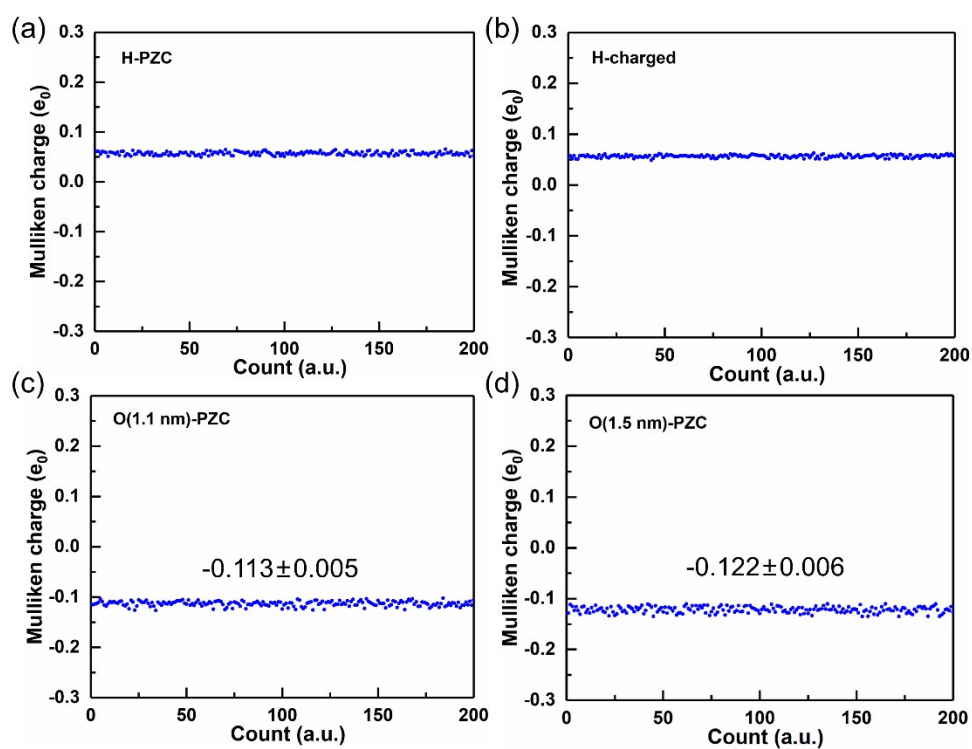


Figure S5. Mulliken charge of (a) passivated H atoms at PZC, (b) passivated H atoms in the interface with one Na charged, (c) passivated O atoms for the pore with the size of 1.1 nm, and (d) passivated O atoms for the pore with the size of 1.5 nm.

Table S1. Calculated work functions (Φ , in eV) of 12 structures of H-pore/electrolyte interface from ab initio molecular dynamics simulations.

Charged	Potential (V vs PZC)			Average potential
	-0.74637	-0.22863	-0.35878	-0.54±0.28
	-0.29283	-0.74921	-0.42112	
	-0.8439	-0.84033	-0.69549	
	-0.21547	-0.69155	-0.81073	

Table S2. Calculated work functions (Φ , in eV) of 12 structures of O-pore/electrolyte interface from ab initio molecular dynamics simulations.

Charged	Potential (V vs PZC)			Average potential
	-0.66131	-0.4675	0.3776	-0.19± 0.38
	0.126115	-0.12083	0.1072	
	0.107203	0.257129	0.238636	
	-0.40738	-0.03103	0.192667	

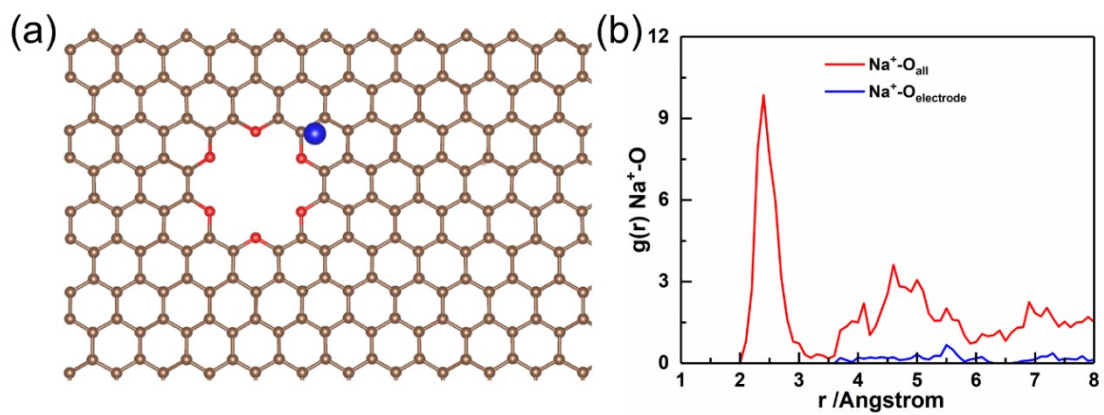


Figure S6. (a) Snapshot of the top view of the O-pore (0.7 nm)/electrolyte interface. (b) Radial distribution function of O atoms in water molecules and at the edge of the pore around Na⁺ at the O-pore (0.7 nm)/electrolyte interface.